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Effects of In-Plane Impurity Substitution in Sr_2RuO_4

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We report comparative substitution effects of *nonmagnetic* Ti^{4+} and *magnetic* Ir^{4+} impurities for Ru^{4+} in the spin-triplet superconductor Sr_2RuO_4. We found that both impurities suppress the superconductivity completely at a concentration of approximately 0.15%, reflecting the high sensitivity to translational symmetry breaking in Sr_2RuO_4. In addition, a rapid enhancement of residual resistivity is in quantitative agreement with unitarity-limit scattering. Our result suggests that both nonmagnetic and magnetic impurities in Sr_2RuO_4 act as strong potential scatterers, similar to the nonmagnetic Zn^{2+} impurity in the high-T_c cuprates.

KEYWORDS: Sr_2RuO_4, impurity effects, unitarity scattering

Unconventional superconductors such as heavy fermion compounds and high-T_c cuprates have attracted much attention in the last two decades, since highly correlated f- and d-electrons in these materials play essential roles in the emergence of the unconventional superconductivity.[1] In contrast to conventional superconductivity with s-wave symmetry, nonmagnetic impurities as well as magnetic impurities act as strong pair breakers and severely suppress the transition temperature T_c of unconventional superconductivity. The suppression of T_c reflects the sensitivity to translational symmetry breaking[2] and is a characteristic of anisotropic pairing. Systematic studies of impurity substitution have also been used to obtain information on the underlying strongly correlated electronic states in both f-[3,4] and d-electron systems.[5]

Here, we study the effects of such substitution in the layered perovskite ruthenate Sr_2RuO_4, whose superconductivity[6] is unconventional, most probably involving spin-triplet pairing.[7] The normal state properties of Sr_2RuO_4 are described quantitatively within the framework of a quasi-two-dimensional Fermi liquid[8] with the Fermi surface consisting of three nearly cylindrical sheets (α, β and γ).[9] Comparison with the band-structure calculation[10] indicates that strong correlations among the electrons originating from the Ru^{4+} ions ($4d^4$ in the low spin configuration) hybridized with p-electrons of surrounding oxygen play an essential role in the physical properties of Sr_2RuO_4.

Early studies of the impurity effects in Sr_2RuO_4 revealed several features reflecting the unconventional superconductivity: rapid suppression of T_c by native impurities and defects[11] and a large enhancement of the residual density of states in the superconducting state seen in specific heat measurements[12] and NMR measurements.[13] Throughout the above series of studies, control of the impurity concentration within the crystals was not easy, because the impurities were introduced accidentally during crystal growth. After considerable effort to optimize the growth conditions,[14] we can now constantly obtain high quality crystals with minimal accidental contamination and $T_c > 1.4$ K. This had allowed us to embark on a systematic study of the effects of controlled substitution of Ru^{4+} with nonmagnetic Ti^{4+} and magnetic Ir^{4+} ions.

The effect of impurity substitution into correlated electron systems can be subtle, with even nonmagnetic ions introducing magnetic effects. Before describing the scattering effects of very low concentrations of Ti^{4+} and Ir^{4+} on the superconductivity, it is therefore useful to review the effects of higher level doping on the magnetic properties. Recently, we reported that the substitution of *nonmagnetic* impurity Ti^{4+} ($3d^0$) in Sr_2RuO_4 induces a local moment with the effective moment $p_{\rm eff} \sim 0.5$ μ_B/Ti.[15] The induced moment has Ising anisotropy with an easy axis along the c direction. Furthermore, magnetic ordering with glassy behavior appears for x(Ti) $\geq 2.5\%$ in $Sr_2Ru_{1-x}Ti_xO_4$ while keeping metallic conduction along the in-plane direction. When x(Ti) is further increased to 9%, *elastic* neutron scattering measurements detect an incommensurate Bragg peak[16] whose wave vector $\boldsymbol{Q}_{\rm ic} \sim (2\pi/3,\ 2\pi/3,\ 0)$ is close to the position of the *inelastic* neutron scattering peak seen in pure Sr_2RuO_4.[17] In the vicinity of the magnetic ordering with $x \geq 2.5\%$, deviation from the Fermi-liquid behavior seen in the pure Sr_2RuO_4 is observed with the resistivity and the specific heat data showing linear-temperature dependence and logarithmic temperature dependence, respectively.[18] These results indicate that the two-dimensional antiferromagnetic spin fluctuations at $\boldsymbol{Q}_{\rm ic}$ arising from the nesting mainly in the β band becomes a static spin density wave (SDW) by *nonmagnetic* Ti substitution.

On the other hand, the system $Sr_2Ru_{1-x}Ir_xO_4$ in which the substitution is *magnetic* Ir^{4+} ($5d^5$ in the low spin configuration) shows weak ferromagnetism at x(Ir)

$\geq$ 30% occurring concomitantly with metal-insulator transition[19] and the end-member material Sr_2IrO_4 is a Mott insulator with canted antiferromagnetic ordering.[20] Thus, substitution of high levels of Ti^{4+} and Ir^{4+} impurities in Sr_2RuO_4 leads to different magnetic ground states, presumably reflecting the different magnetic character of the isolated ions.

In this letter, we show that both nonmagnetic Ti^{4+} and magnetic Ir^{4+} impurities suppress the superconductivity of Sr_2RuO_4 completely by a concentration of $\sim$ 0.15%. Also, both impurities act as strong potential scatterers with the maximum phase shift $\delta_0 \sim \pi/2$ (unitarity limit), as seen in high-T_c cuprates with *nonmagnetic* Zn^{2+} ($3d^{10}$) impurity.

A series of single crystals of $Sr_2Ru_{1-x}Ti_xO_4$ and $Sr_2Ru_{1-x}Ir_xO_4$ with x up to 3% were grown by a floating-zone method with an infrared image furnace (NEC Machinery, model SC-E15HD). The detailed procedure of the crystal growth is described elsewhere.[14,15] We only note here that an excess of 0.15 molar Ru was added for each 2 molar Sr for the crystal growth. The Ti and Ir concentrations in grown crystals were analyzed by electron-probe microanalysis (EPMA). The Ti is well substituted for Ru as reported by Minakata and Maeno.[15] On the other hand, we found that the Ir as well as Ru was heavily evaporated during crystal growth at the high temperature of ~2200 °C, so that excess amounts had to be added for the crystal growth: the analyzed Ir concentration x_a(Ir) is roughly connected with the nominal concentration x_n(Ir) by $x_a \sim 0.25x_n$ for $x_n \leq 9\%$. We note that the tetragonal crystal symmetry[15,19] for both $Sr_2Ru_{1-x}Ti_xO_4$ and $Sr_2Ru_{1-x}Ir_xO_4$ with x up to 3% was confirmed at room temperature. The induced moment by magnetic impurities is *isotropic* in sharp contrast to the result of Ti substituted system and estimated as 0.7 μ_B/Ir from susceptibility measurements. This value is much smaller than the previous report using polycrystals, ~2 μ_B/Ir at x(Ir) $\sim$ 5%.[19]

For the resistivity measurements, the crystals were cut into rectangles with a typical size of 3.5 × 0.4 × 0.05 mm^3. The shortest dimension was along the c axis. Silver paste (Dupont, 6838) was used for attaching electrodes and cured at 500 °C for 5 minutes; the contact resistances were below 0.4 Ω. The in-plane resistivity ρ_{ab} measurements were performed by a standard four-probe dc method between 4.2 and 300 K and by a low frequency ac method between 0.3 and 5 K. Before measuring the ρ_{ab} of $Sr_2Ru_{1-x}Ti_xO_4$ and $Sr_2Ru_{1-x}Ir_xO_4$, we examined the absolute value of the ρ_{ab} for Sr_2RuO_4 crystals without Ti and Ir substitutions but with various T_c (1.42 K, 1.24 K and less than 0.3 K) in order to remove the uncertainty due to the size error and the inhomogeneous current path. The resistivity of these crystals were 121 ± 2 $\mu\Omega$cm at 300 K. Moreover, the residual resistivity ρ_{ab0} were 0.15, 0.40 and 1.6 $\mu\Omega$cm, respectively, in the order of decreasing T_c. Here, the ρ_{ab0} was defined by the extrapolation of the the low temperature resistivity to $T = 0$. The T_c vs. ρ_{ab0} agreed well with the previous data.[11]

Figure 1 shows the temperature dependence of ρ_{ab} in $Sr_2Ru_{1-x}Ti_xO_4$ and $Sr_2Ru_{1-x}Ir_xO_4$ with a small amount of x. The T_c is rapidly and systematically suppressed in both cases. The result reflects the high sensitivity to translational symmetry breaking, characteristic of unconventional superconductivity. The inset shows the dependence of T_c on the impurity concentration x. We can see an almost universal suppression of T_c, irrespective of the kind of impurity. The broken line shows the universal Abrikosov-Gor'kov pair-breaking function, where the formulation is generalized to the case of nonmagnetic and magnetic impurities in an unconventional superconductor.[21] Based on this model, $T_c(x)$ satisfies

$$\ln\left(\frac{T_c}{T_{c0}}\right) = \Psi\left(\frac{1}{2}\right) - \Psi\left(\frac{1}{2} + \frac{\hbar\Gamma}{2\pi k_B T_c}\right).$$

Here Ψ is the digamma function, $\hbar$ the Dirac constant and the scattering rate $\Gamma = \dfrac{1}{2\tau} = \dfrac{2x}{\pi\hbar N_0}\sin^2\delta_0 + AS(S+1)$; the first and second terms in Γ represent the potential and magnetic spin-flip scattering contributions, respectively, where N_0 is the density of states in the normal state. From our best fitting by fixing T_{c0} as 1.5 K, the initial rate $dT_c/dx \sim -7.5$ K/x(%) is obtained for both Ti and Ir substitutions. The critical concentration x_c for disappearance of the superconductivity is estimated as $x_c \sim 0.15\%$.

By measuring the residual resistivity ρ_{ab0} (Fig. 1), we can see a universal trend that the superconductivity of Sr_2RuO_4 is completely suppressed at the critical resistivity of $\rho_{ab0} \sim 1.1$ $\mu\Omega$cm for both impurities, as reported from previous studies with native impurities and defects.[11] The critical value ρ_{ab0} is again in good agreement with the mean free path l_{ab} falling below the superconducting coherence length $\xi_{ab} \sim 900$Åwhen superconductivity is destroyed.

The fact that Ti^{4+} and Ir^{4+} suppress T_c in the same way in spite of their very different magnetic characters suggests that the magnetic contribution to pair breaking is negligible, and potential scattering dominates. Although it could also be explained in other ways, this observation is qualitatively consistent with the existence of a spin-triplet state. Magnetic impurities break singlet pairs essentially because of exchange splitting of the single particle state; equal spin paired triplet states would not be subject to such an effect. Similar observations of negligible magnetic pair breaking have also been reported in UPt_3.[3]

In Fig. 2, the impurity concentration dependence of ρ_{ab0} is displayed for $Sr_2Ru_{1-x}Ti_xO_4$ and $Sr_2Ru_{1-x}Ir_xO_4$. The enhancement of ρ_{ab0} shows the same behavior for both impurities with a slope $d\rho_{ab0}/dx$ $\sim$ 500 $\mu\Omega$cm/x. For potential scattering, the residual resistivity in a two dimensional system is given as

$$\rho_{ab0} = \frac{4\hbar}{e^2}\frac{x}{\sum_i^{\alpha,\beta,\gamma} n_i}\sin^2\delta_0,$$

where, n_i is the carrier concentration for each Fermi surface (α,β,γ).[9] Using the relation $n_i = k_{Fi}^2/2\pi d$, where k_{Fi} is each Fermi wave number in cylindrical Fermi surface approximation[9] and d the interlayer distance, we can obtain $d\rho_{ab0}/dx = 425$ $\mu\Omega$cm/x in Sr_2RuO_4, drawn as a broken line in Fig. 2. Here we have assumed the

unitarity limit, namely with the maximum phase shift $\delta_0 = \pi/2$. The estimated value is in good agreement with the experimental results. Also, by assuming *only* potential scattering contribution with $\delta_0 = \pi/2$, we estimated $\dfrac{\mathrm{d}T_\mathrm{c}}{\mathrm{d}x} = -\dfrac{\pi\hbar\mathit{\Gamma}}{2k_\mathrm{B}}\dfrac{1}{x} \sim -10$ K$/x(\%)$ and the critical concentration for disappearance of the superconductivity $x_\mathrm{c} \sim \dfrac{\pi^2 k_\mathrm{B} T_{\mathrm{c}0} N_0}{4\gamma}\dfrac{1}{\sin^2\delta_0} \sim 0.1\%$. Here, γ is the Euler constant. These values are consistent with the experimental values ~ -7.5 K$/x\%$ and $\sim 0.15\%$, respectively. These results again suggest that both nonmagnetic and magnetic impurities act mainly as strong potential scatterers in Sr_2RuO_4. This unitarity scattering in Sr_2RuO_4 is similar to the substitution effect of nonmagnetic (Zn^{2+}) impurity in high-T_c cuprates.[5)]

Table I summarizes the nonmagnetic and magnetic substitution effects in Sr_2RuO_4, in comparison with those in the high-T_c cuprates. For both impurities, further substitution leads to different magnetic ground state, namely spin glass behavior coexisting with incommensurate magnetic order[15, 16)] and weak ferromagnetism[19, 20)] for nonmagnetic and magnetic impurities, respectively. At very low doping levels, however, we have shown here that both impurities have very similar effects on transport and magnetic properties. In order to clarify the similarity and the difference in more detail, it is very important to investigate how the spin fluctuation at $\boldsymbol{Q}_\mathrm{ic}$ is modified by the magnetic impurity, as has been done for the nonmagnetic impurity.[16)]

In summary, we report systematic comparison of the substitution effects of *nonmagnetic* and *magnetic* impurities in the spin-triplet superconductor Sr_2RuO_4. Irrespective of leading to different magnetic ordering at high levels of substitution, we found universal behavior for both impurities in the suppression of T_c and the enhancement of ρ_{ab0}, in accordance with the strong potential scattering with $\delta_0 = \pi/2$. Our result suggests that both nonmagnetic and magnetic impurities in Sr_2RuO_4 break pairs due to strong potential scattering, and that magnetic scattering does not play an important role.

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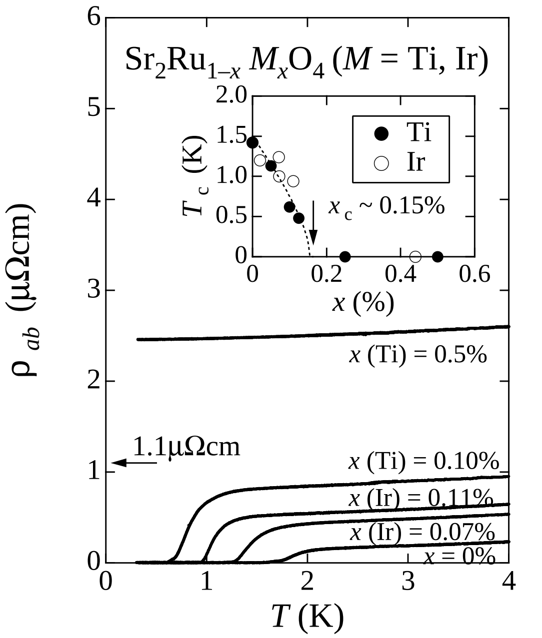

Fig. 1. Temperature dependence of the in-plane resistivities ρ_{ab} in $Sr_2Ru_{1-x}Ti_xO_4$ and $Sr_2Ru_{1-x}Ir_xO_4$. Inset: Superconducting transition temperature T_c as a function of the impurity concentration x. The broken line shows the best fitting by Abrikosov-Gor'kov pair-breaking function.

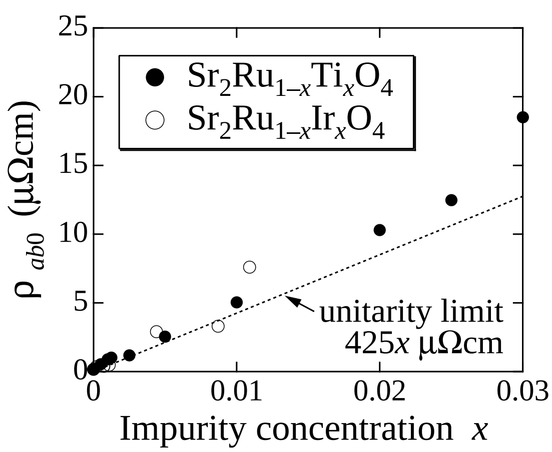

Fig. 2. Residual resistivity ρ_{ab0} as a function of x for $Sr_2Ru_{1-x}Ti_xO_4$ and $Sr_2Ru_{1-x}Ir_xO_4$. The broken line represents the unitarity scattering with the phase shift $\delta_0 = \pi/2$.

Table I. Substitution effects of nonmagnetic and magnetic impurity in (a) Sr_2RuO_4, (b) underdoped and (c) overdoped cuprates.

(a) Sr_2RuO_4

	$Sr_2Ru_{1-x}Ti_xO_4$	$Sr_2Ru_{1-x}Ir_xO_4$
phase shift (δ_0)	$\pi/2$	$\pi/2$
p_{eff}	0.5 μ_B/Ti[15]	0.7 μ_B/Ir
magnetic order	x(Ti) $\geq$ 2.5%[15]	x(Ir) $\geq$ 30%[19]
	SDW and spin glass	weak ferromagnetism[19]

(b) high-T_c cuprates (underdoped)

	nonmagnetic (Zn^{2+})	magnetic (Ni^{2+})
phase shift (δ_0)	$\pi/2$[5]	0.36π[5]
p_{eff}	1 μ_B/Zn[22]	1.6 μ_B/Ni[22]
magnetic order	–	–

(c) high-T_c cuprates (overdoped)

	nonmagnetic (Zn^{2+})	magnetic (Ni^{2+})
phase shift (δ_0)	$\pi/2$[5]	0.32 - 0.36π[23]
p_{eff}	0.4 μ_B/Zn[22]	1.2 μ_B/Ni[22]
magnetic order	–	–